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Effect of Divalent Ions on the Structure of Organic Langmuir Monolayers

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Introduction: Studies of interactions between simple carboxylic head groups and aqueous ion complexes may provide new insights into understanding template-directed inorganic nucleation phenomena [1]. There are now multiple reports of superlattice reflections in GID patterns of inorganic-organic Langmuir systems [2,3], but the interpretation of what they are due to is not entirely clear. To test the conventional interpretation that superlattice peaks are an indication of an ordered inorganic lattice, we have performed a GID study (including Bragg rod scans) on Langmuir films of heneicosanoic acid on a subphase with dilute solutions of magnesium chloride.

Methods and Materials: We have performed grazing incidence x-ray diffraction on Langmuir monolayers of heneicosanoic fatty acid (C_{21}) with magnesium chloride in the aqueous subphase. The concentration was 10^{-4}M and pH was adjusted to 8 with sodium hydroxide. The monolayer was compressed to slightly above zero dynes/cm pressure and held at temperature of 10°C.

Results: In addition to organic peaks, the in-plane scan of the film reveals a 2x2 superlattice (not shown). The bragg rods along these superlattice peaks were fitted with a profile calculated from the structure factor. Fatty acid molecules in their untilted structure can be approximately treated as upright cylindrical rods of length L_{org}, and in this approximation, the intensity profile of a Bragg rod is given by $I_{hk}(K_z) \approx I_0 \sin(N \cdot W)^2 / \sin(W)^2$, where $W = d \cdot K_z / 2$ and $L_{org} = d \cdot N$ and one expects secondary oscillations in such profiles. The primary and two or three subsidiary maxima are seen in Bragg rods of the organic peaks for the film with magnesium and also for C_{21} on pure water (bragg rods are shown only for Mg). The oscillations are always consistent with a thickness of 27Å, the length of the heneicosanoic acid molecule. As in the organic Bragg rod, small secondary maxima (oscillations) are also clearly seen in Bragg rod profiles of the superlattice peaks (Figure, top, a-d), but these profiles lack the strong 'primary maximum.' There is no reason to expect that the ordered subphase layer will be as thick as the inorganic film. The spacing between oscillations is roughly the same for organic peaks and superlattice peaks, which is quite unexpected: a thin layer of ions would result in a featureless Bragg rod as in Figure 6a (right). If there were no ordered inorganic layer under the Langmuir monolayer and the organic film had an out-of-plane density modulation ("buckling"---as shown schematically in Figure 2a (left)) with the periodicity of the superlattice, an oscillation in the profile of superlattice Bragg rods would be seen as in Figure 2b (right). The Bragg rods we observe do not look like either one of the previous cases, but are a combination of both, as in Figure 2c (right). We must therefore conclude that the observed superlattice Bragg rods contain a contribution from an ordered inorganic lattice *as well as* buckling in the organic film. Our calculations show that in order to fit the Bragg rods, there must be an ordered layer of subphase atoms, and that the organic film must also buckle. The best fits were achieved with a chain-chain offset h_{pr} = 2.5 Å, which is close to 2 times the C-C spacing in the hydrocarbon chain, and with an inorganic layer of thickness L_{inorg} ~ 4 Å. We have found similar oscillations in Bragg rods with film with other ions that give superlattice peaks (Mn^{2+}, Pb^{2+}, Cd^{2+})

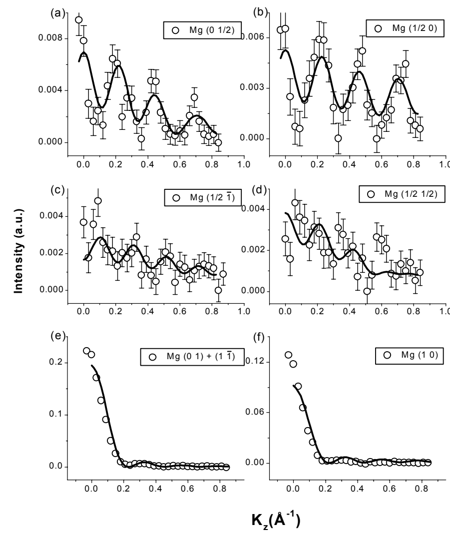

Figure 1. Bragg rod scans of six in-plane peaks on a film with $MgCl_2$: (top) Along superlattice 'inorganic' peaks (0 ½), (½ 0), (½ $\bar{1}$), and (½ ½). All four Bragg rods were fitted simultaneously, that is, one set of parameters produced all six curves (bottom) Along peaks due to the organic monolayer (0 1)+(1 $\bar{1}$) and (1 0).

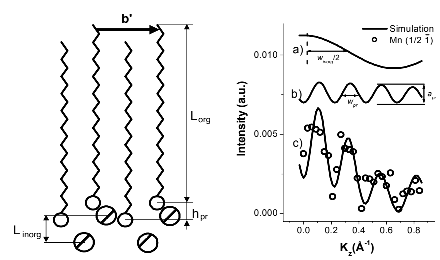

Figure 2. (Left) A model of periodic protrusions of aliphatic chains. In a cross-section along the super cell vector **b**, every other molecule is vertically displaced by an amount h_{pr}. Four subphase atoms are placed in a box under the organic film (only two subphase atoms per supercell are shown). (Rright) Simulations of Bragg rods: (a) with subphase atoms under an unbuckled organic film. (b) with periodic protrusions of organic chains (buckling) and no subphase atoms under the organic film. (c) with both an ordered inorganic layer and periodic protrusions of organic chains.

Conclusions: Some ions form superlattices and some do not, and the superlattices are partially due to periodic modulations of the organic molecules. Periodic modulations have been observed on solid substrates, but this is the first time such periodic modulations have been observed on a water surface.

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References: [1] S. Mann et al., Science **261**, 1286 (1993); [2] F. Leveiller et al., Langmuir **10**, 819 (1994); [3] J. Kmetko et al., Langmuir **17**, 4697 (2001)